

Title**Titanocene-based catalyst system**

The present invention relates to a solid catalyst system comprising a metallocene containing titanium as central metal (titanocene) and a partially dealcoholated adduct of magnesium dihalide and alcohol.

The use of metallocene compounds and, in particular, titanocene compounds as catalyst components for the polymerization of olefins is well known in the art. They are usually used in conjunction with alumoxanes as cocatalysts. The catalyst systems comprising titanocene compounds and alumoxanes can be used supported on an inert support in order to control the morphology of the obtained polymer and to avoid fouling in the reactor, especially in a gas-phase or slurry polymerization processes.

The drawback of the catalyst systems so obtained is that since alumoxanes need to be used in large excess with respect to titanocene compounds the resulting catalyst is very expensive. Therefore it is desirable to reduce or eliminate the use of alumoxanes.

Magnesium chloride is a well-known support for Ziegler-Natta based catalyst systems containing titanium halide. The use of this compound as a carrier for single-site catalysts could be very advantageous, in view of its chemical and structural simplicity, and to the possibility to finely control the porosity of this support and, therefore, to easily tune the porosity of the final catalyst system.

Several catalyst systems trying to solve the problem of the use of alumoxanes in a magnesium halide supported catalyst system have been proposed in the art.

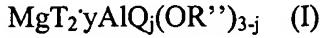
For example in Macromol. Chem. Phys. 195, 1369-1379 (1984) $MgCl_2$ in combination with a zirconocene catalyst and trialkylaluminum is used. More recently, In Macromolecules 1993, 26, 4712 mixtures of MgR_2 and AlR_2Cl (generating $MgCl_2$ and AlR_3) as cocatalyst components for olefin polymerization using various metallocenes have been used. In various papers, namely, Korean J. Chem. Eng. 16(5) 562-570, Journal of Applied Polymer science Vol 70, 1707-1715, Korean J. Chem. Eng. 19(4) 557-563 and J. Molec. Catal A 191, 2003, 155-165 Lee and co-workers, proposed a metallocene-based catalyst system in which alcohol and anhydrous $MgCl_2$ are reacted to form an adduct $MgCl_2$ -alcohol. The adduct, further reacted with trialkylaluminum, is used for supporting zirconocene compounds. The obtained catalyst system can be used without a further addition of alumoxanes.

In all these documents only metallocene compounds in which the central metal is zirconium have been used, moreover the adduct $MgCl_2$ alcohol used is not dealcoholated and it is not characterized by particular values of porosity and surface area. As shown in the comparative tests of the present application the use of a dealcoholated adduct of magnesium halide and alcohol improves the activity of the titanium-based catalyst system. US 5698487 relates to a magnesium halide having a surface area (BET) greater than 50 m^2/g , porosity (BET) greater than 0.15 cm^3/g and porosity (Hg) greater than 0.3 cm^3/g . The adduct $MgCl_2$ -alcohol having these features has been used in combination with trialkylaluminum or alumoxane for supporting metallocene compounds. In all the working examples the metallocene compound is combined with trialkylaluminum or alumoxane before contact with the above support. As shown in the comparative test of the present application when the titanocene is not prereacted with trialkylaluminum the polymerization activity of the resulting catalyst system is improved.

The object of the present invention is a catalyst system obtainable by the process comprising the following steps:

- a) contacting
 - (i) a partially dealcoholated adduct of formula $MgT_2 \cdot wR'OH$ wherein T is chlorine, bromine, or iodine, preferably chlorine; R' is a linear or branched C_1-C_{10} alkyl radical, preferably R' is a linear C_1-C_{10} alkyl radical; more preferably R' is a methyl or an ethyl radical; w ranges from 3 to 0.1, preferably from 3 to 0.5; more preferably from 3 to 1 being also a non integer number; with
 - (ii) an organo-aluminium compound of formula H_eAlU_{3-e} or $H_eAl_2U_{6-e}$, wherein each U substituent, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing silicon or germanium atoms; with the proviso that at least one U is different from halogen, and e ranges from 0 to 1, being also a non-integer number; preferably said hydrocarbon radicals are linear or branched, cyclic or acyclic, C_1-C_{20} -alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_6-C_{20} -aryl, C_7-C_{20} -alkylaryl or C_7-C_{20} -arylalkyl radicals optionally containing silicon or germanium atoms; preferably U is a linear or branched C_1-C_{20} -alkyl radical; more preferably U is an ethyl, a n-propyl, a iso propyl, a n-butyl, a iso-butyl, a tert-butyl, a hexyl or an octyl radical;

to obtain an adduct of formula (I)



wherein

y ranges from 1.00 to 0.05;

Q has the same meaning of U hydrogen and halogen atoms being excluded;

R'' has been described above

and j ranges from 0.01 to 3.00, being also a non-integer number.

b) contacting the product obtained from step a) with at least one metallocene compound having titanium as central metal and at least one ligand having a cyclopentadienyl skeleton;

with the proviso that the metallocene compound of step b) is not previously treated with an organo-aluminium compound of formula H_eAlU_{3-e} or $H_eAl_2U_{6-e}$, or with an alumoxane.

In step a) the product obtained by combining the partially dealcoholated adduct of formula $MgT_2^wR'OH$ and organo-aluminium compound of formula H_eAlU_{3-e} or $H_eAl_2U_{6-e}$, (ii) is an adduct of formula (I)

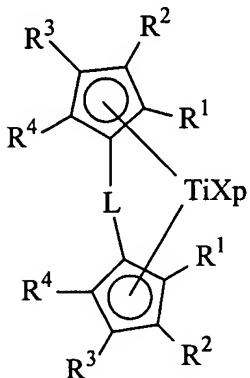


preferably in the compound of formula (I) y ranges from 0.50 to 0.10; more preferably it ranges from 0.40 to 0.10;

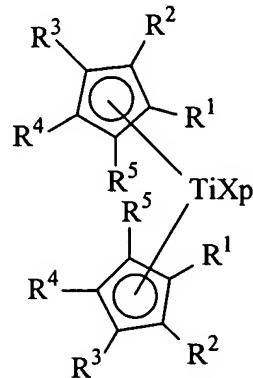
j preferably ranges from 2.50 to 2.00; more preferably it ranges from 2.50 to 2.20.

Preferably said adduct of formula (I) has a surface area (BET) higher than $30 \text{ m}^2/\text{g}$; more preferably higher than $38 \text{ m}^2/\text{g}$; even more preferably higher than $200 \text{ m}^2/\text{g}$; but it can reach values higher than $300 \text{ m}^2/\text{g}$.

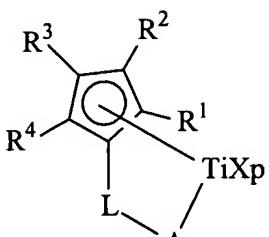
A preferred class of metallocene compounds to be used in step b) belongs to the following formulas (II), (III), (IV) or (V)



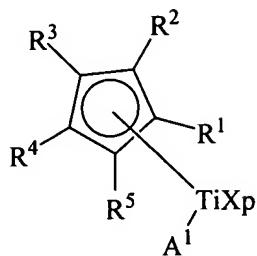
(II)



(III)



(IV)



(V)

wherein

Ti is titanium;

the substituents X, equal to or different from each other, are monoanionic sigma ligands selected from the group consisting of hydrogen, halogen, R^6 , OR^6 , $OCOR^6$, SR^6 , NR^6_2 and PR^6_2 , wherein R^6 is a hydrocarbon radical containing from 1 to 20 carbon atoms optionally containing one or more Si or Ge atoms; preferably R^6 is a linear or branched, cyclic or acyclic, C_1-C_{20} -alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_6-C_{20} -aryl, C_7-C_{20} -alkylaryl or C_7-C_{20} -arylalkyl optionally containing one or more Si or Ge atoms;

the substituents X are preferably the same and are preferably halogen, R^6 , OR^6 and NR^6_2 ; wherein R^6 is preferably a C_1-C_7 alkyl, C_6-C_{14} aryl or C_7-C_{14} arylalkyl group, optionally containing one or more Si or Ge atoms; more preferably, the substituents X are selected from the group consisting of -Cl, -Br, -Me, -Et, -n-Bu, -sec-Bu, -Ph, -Bz, - CH_2SiMe_3 , -OEt, -OPr, -OBu, -OBz and -NMe₂; more preferably X is Cl or Me.

p is an integer ranging from 1 to 2;

L is a divalent bridging group selected from C_1-C_{20} alkylidene, C_3-C_{20} cycloalkylidene, C_6-C_{20} arylidene, C_7-C_{20} alkylarylidene, or C_7-C_{20} arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms such as $SiMe_2$, $SiPh_2$; preferably L is a divalent group $(ZR^7_m)_n$; Z being C, Si, Ge, N or P, and the R^7 groups, equal to or different from each other, being hydrogen or hydrocarbon groups containing from 1 to 20 carbon atoms, or two R^7 can form a aliphatic or aromatic C_4-C_7 ring; preferably R^7 is hydrogen or a linear or branched, cyclic or acyclic, C_1-C_{20} -alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_6-C_{20} -aryl, C_7-C_{20} -alkylaryl or C_7-C_{20} -arylalkyl radical;

more preferably L is selected from $Si(CH_3)_2$, $SiPh_2$, $SiPhMe$, $SiMe(SiMe_3)$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$;

m is 1 or 2, and more specifically it is 1 when Z is N or P, and it is 2 when Z is C, Si or Ge;

n is an integer ranging from 1 to 4; preferably it is 1 or 2;

each R¹, R², R³, R⁴ and R⁵, equal to or different from each other, is a hydrogen atom, a C₁-C₄₀ hydrocarbon group optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R¹, R², R³, R⁴ and R⁵ form one or more 3-7 membered ring optional containing heteroatoms belonging to groups 13-17 of the periodic table; such as to form with the cyclopentadienyl moiety the following radicals: indenyl; mono-, di-, tri- and tetra-methyl indenyl; 2-methyl indenyl, 3-butyl-indenyl, 2-isopropyl-4-phenyl indenyl, 2-methyl-4-phenyl indenyl, 2-methyl-4,5 benzo indenyl; 3-trimethylsilyl-indenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; 5,10-dihydroindeno[1,2-b]indol-10-yl; N-methyl- or N-phenyl-5,10-dihydroindeno [1,2-b]indol-10-yl; 5,6-dihydroindeno[2,1-b]indol-6-yl; N-methyl- or N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalene-4-yl; azapentalene-6-yl; thiapentalene-6-yl; mono-, di- and tri-methyl-azapentalene-4-yl, 2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene; preferably each R¹, R², R³, R⁴ and R⁵ is a hydrogen atom or a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two adjacent R¹, R², R³, R⁴ and R⁵ form one or more 3-7 membered ring optional containing heteroatoms belonging to groups 13-17 of the periodic table;

A is a NR⁸, O, S radical, wherein R⁸ is a C₁-C₂₀ hydrocarbon group optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R⁸ is a linear or branched, cyclic or acyclic, C₁-C₂₀-alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R⁸ is tert-butyl.

A¹ is a hydrogen atom, a halogen atom, R⁶, OR⁶, OCOR⁶, SR⁶, NR⁶₂ and PR⁶₂, wherein R⁶ is as described above; or A¹ is a NR⁹ radical wherein R⁹ is a C₁-C₄₀ hydrocarbon group optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

Non limiting examples of compounds belonging to formulas (II), (III), (IV) and (V) are the following compounds (when possible in either their meso or racemic isomers, or mixtures thereof):

bis(cyclopentadienyl)titanium dichloride;

bis(indenyl)titanium dichloride;

bis(tetrahydroindenyl)titanium dichloride;
bis(fluorenyl)titanium dichloride;
(cyclopentadienyl)(indenyl)titanium dichloride;
(cyclopentadienyl)(fluorenyl)titanium dichloride;
(cyclopentadienyl)(tetrahydroindenyl)titanium dichloride;
(fluorenyl)(indenyl)titanium dichloride;
dimethylsilanediylbis(indenyl)titanium dichloride,
dimethylsilanediylbis(2-methyl-4-phenylindenyl)titanium dichloride,
dimethylsilanediylbis(4-naphthylindenyl)titanium dichloride,
dimethylsilanediylbis(2-methylindenyl)titanium dichloride,
dimethylsilanediylbis(2-methyl-4-t-butylindenyl)titanium dichloride,
dimethylsilanediylbis(2-methyl-4-isopropylindenyl)titanium dichloride,
dimethylsilanediylbis(2,4-dichlorideindenyl)titanium dichloride,
dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)titanium dichloride,
dimethylsilanediylbis(2,4,7-trimethylindenyl)titanium dichloride,
dimethylsilanediylbis(2,4,6-trimethylindenyl)titanium dichloride,
dimethylsilanediylbis(2,5,6-trimethylindenyl)titanium dichloride,
methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-titanium dichloride,
methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)-titanium dichloride,
1,2-ethylenebis(indenyl)titanium dichloride,
1,2-ethylenebis(4,7-dichlorideindenyl)titanium dichloride,
1,2-ethylenebis(2-methyl-4-phenylindenyl)titanium dichloride,
1,4-butanediylbis(2-methyl-4-phenylindenyl)titanium dichloride,
1,2- ethylenebis(2-methyl-4,6-diisopropylindenyl)titanium dichloride,
1,4-butanediylbis(2-methyl-4-isopropylindenyl)titanium dichloride,
1,4-butanediylbis(2-methyl-4,5-benzoindenyl)titanium dichloride,
1,2- ethylenebis (2-methyl-4,5-benzoindenyl)titanium dichloride,
[4-(η^5 -cyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydro-pentalene)]dichloridetitanium,
[4-(η^5 -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydropentalene)]dichloridetitanium,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-dichloridetitanium,
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)dichloridesilyl-dichloridetitanium,
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyl-dichloridetitanium,

(tertbutylamido)-(2,4-dichloride-2,4-pentadien-1-yl)dimethylsilyl-dichloridetitanium, bis(1,3-dichloridecyclopentadienyl)titanium dichloride, methylene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)titanium dichloride; methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)titanium dichloride; methylene(2,4-dichloride-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)titanium dichloride; methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)titanium dichloride; methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; methylene-1-(indenyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; methylene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; methylene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; methylene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)titanium dichloride; methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)titanium dichloride; methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dioxazol)titanium dichloride; isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride; isopropylidene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride;

isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)titanium dichloride;

isopropylidene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride;

isopropylidene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride;

dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)titanium dichloride;

dimethylsilanediyl(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, dimethylsilanediyl(3-isopropyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, dimethylsilanediyl(3-methyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, dimethylsilanediyl(3-ethyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, 1-2-ethane(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, 1-2-ethane (3-isopropyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, 1-2-ethane (3-methyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, 1-2-ethane (3-ethyl-cyclopentadienyl)(9-fluorenyl)titanium dichloride, dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-thiophene) dichloride; dimethylsilandiylbis-6-(4-methylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-(4-isopropylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-(4-tert-butylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-(2,5-methyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride; dimethylsilandiylbis-6-[2,5-dimethyl-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-thiophene]titanium dichloride; dimethylsilandiylbis-6-[2,5-dimethyl-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-thiophene]titanium dichloride; dimethylsilandiylbis-6-[2,5-dimethyl-3-mesitylenecyclopentadienyl-[1,2-b]-thiophene]titanium dichloride;

dimethylsilandiylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride;

dimethylsilandiylbis-6-(2,5-diethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride;

dimethylsilandiylbis-6-(2,5-diisopropyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride;

dimethylsilandiylbis-6-(2,5-diter-butyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride;

dimethylsilandiylbis-6-(2,5-dtrimethylsilyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)titanium dichloride;

dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-silole)titanium dichloride;

dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-silole)titanium dichloride;

dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-silole)titanium dichloride;

dimethylsilandiylbis-6-(2,5-dichloride-3-phenylcyclopentadienyl-[1,2-b]-silole)titanium dichloride;

dimethylsilandiylbis-6-[2,5-dichloride-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-silole]titanium dichloride;

dimethylsilandiylbis-6-[2,5-dichloride-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-silole]titanium dichloride;

dimethylsilandiylbis-6-[2,5-dichloride-3-mesilylenecyclopentadienyl-[1,2-b]-silole]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(6-methyl-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(6-methoxy-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(N-ethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

[dimethylsilyl(tert-butylamido)][(6-methyl-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(6-methoxy-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-methyl-3,4-dichloride-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-ethyl-3,4-dichloride-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-phenyl-3,4-dichloride-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;

as well as the corresponding dimethyl, hydrochloro and dihydro compounds.

Suitable metallocene complexes belonging to formulas (II), (III) (IV) and (V) are described in WO 98/22486, WO 99/58539 WO 99/24446, US 5,556,928, WO 96/22995, EP-A-485 822, EP-A-485 820, US 5,324,800, EP-A-129 368, US 5,145,819, EP-A-485 823, WO 01/47939, WO 01/44318, PCT/EP02/13552, EP-A-416 815, EP-A-420 436, EP-A-671 404, EP-A-643 066 and WO 91/04257.

The partially dealcoholated adduct of formula $MgT_2 \cdot wR'OH$ used in step a) can be obtained by partial dealcoholation of adducts of MgT_2 with alcohols, said adducts containing from 1 to 6 mol of alcohol. It is possible that two adducts having the same content of alcohol, i.e. having the same brute formula, be different in porosity and surface area for the reason that one adduct is partially dealcoholated.

The dealcoholation can be carried out according to known methodologies such as those described in EP-A-395 083. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 3 moles of alcohol per mole of MgT_2 , preferably from 2.9 to 0.5; more preferably from 2.9 to 1.

Said partially dehalcoholated magnesium adduct is then contacted with an organo-aluminium compound of formula H_eAlU_{3-e} or $H_eAl_2U_{6-e}$ in an inert solvent by using methods common known in the art, such as the method described in EP-A-553 806.

In step b) of the process of the present invention the titanocene compound can be supported on the carrier obtained in step a) according to known methods by bringing the product of step a) into contact, for example, with a solution of the titanocene compound,

operating at temperatures between room temperature and 120°C. The metallocene compound that is not fixed on the support is removed by filtration or similar methods.

The amount of titanocene compound supported on the adduct of formula (I) is generally between 1000 $\mu\text{mol/g}$ of support and 1 $\mu\text{mol/g}$ of support; preferably said amount ranges from 500 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support; more preferably from 200 $\mu\text{mol/g}$ of support to 2 $\mu\text{mol/g}$ of support.

The catalyst system object of the present invention can be used for (co)polymerizing one or more olefins. Therefore a further object of the present invention is a process for (co)polymerizing olefins containing from 2 to 20 carbon atoms comprising contacting one or more of said olefins under polymerization conditions in the presence of the catalyst system described above. Preferably alpha-olefins containing from 2 to 20 carbon atoms are used.

Examples of alpha-olefins that can be used with the process of the present invention are: ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred olefins are propylene, ethylene 1-butene, 1-hexene and 1-octene.

The following examples are given for illustrative purpose and do not intend to limit the invention.

Materials and general procedures

All manipulations were performed under an argon atmosphere using a glove box (Braun MB-150 GI or LM-130) and Schlenk techniques. Solvents were distilled from Na (toluene) or Na/benzophenone (heptane) and freeze-thaw degassed twice before use.

Cp_2TiCl_2 and Cp_2ZrCl_2 were purchased from Aldrich and recrystallised from toluene and dichloromethane respectively prior to use.

rac-Ethylenebis(indenyl)zirconium dichloride ($\text{Et}[\text{Ind}]_2\text{ZrCl}_2$) was prepared according to F.R.W.P. Wild, L. Zsolnai, G. Huttner, H.H. Brintzinger, *J. Organomet. Chem.* 1982, 232, 233.

$\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}'\text{Bu})\text{TiCl}_2$ was prepared according to EP 416815.

$\text{Cp}[1,3-(2',6'-\text{Me}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2$ was prepared according to WO 02/070569.

$(\text{N}'\text{Bu}_3\text{P}=\text{N})\text{Cp}\text{TiCl}_2$ was prepared according to D.W. Stephan, J.C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R.E.v.H. Spence, W. Xu, L. Koch, X. Gao, D.G. Harrison, *Organometallics*, 2003, 22, 1937.

CpTiCl_3 was prepared according to A.N. Cardoso, R.J.H. Clark, S. Moorhouse, *J. Chem. Soc., Dalton Trans.* **1980**, 7, 1156.

$(^t\text{BuCp})\text{TiCl}_3$ was prepared according to K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules*, **1998**, 33, 7588.

$(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3$ was prepared according to J. Saßmannshausen, A.K. Powell, C.E. Anson, S. Wocadlo, M. Bochmann, *J. Organometal. Chem.* **1999**, 592, 84.

AlEt_3 (25 wt.% solution in toluene) and AlEt_2Cl (25 wt. % solution in toluene) were obtained from Aldrich, whilst Al^iBu_3 (1M solution in hexane) was purchased from Fluka.

Ethylene (3.5 grade supplied by Air Liquide) was purified by passing over columns of 4 \AA Molecular Sieves and BTS copper catalyst.

The Al and transition metal contents were determined by atomic absorption.

Surface area (BET) is determined according to BET methods (apparatus used: SORPTOMATIC 1800 from Carlo Erba).

The ethoxide content in the magnesium adducts was determined by GC analysis of the ethanol content of a solution obtained by dissolving 100 mg support in 5 mL *n*-BuOH containing a known quantity of *n*-PrOH as internal standard.

Preparation of partially dealcoholated adduct of formula $\text{MgCl}_2 \cdot w\text{ROH}$

The adduct $\text{MgCl}_2 \cdot 3\text{EtOH}$ was prepared according to the procedure described in Example 2 of Patent U.S. Pat. No. 4,399,054, operating at 3000 rpm instead of at 10000 rpm.

The adduct was partially dealcoholated by heating in a stream of nitrogen at temperatures increasing from 30°C. to 180°C., until an adduct containing the amount of ethyl alcohol reported in table 1 was obtained.

Preparation of the catalyst system, general procedure

step a) preparation of the support $\text{MgCl}_2/\text{AlR}_i(\text{OEt})_{3-i}$

Typically, 10 mL *n*-heptane were added to 1 g of a adduct of magnesium chloride and ethanol prepared according to the procedure reported above under argon and the mixture was cooled to 0 °C. A 25 wt-% solution in the solvent indicated in table 1 of the organo-aluminium compound reported in table 1 was then added gradually, over 5-10 min. in a mol ratio Al/EtOH reported in table 1. The reaction being carried out in a standard Schlenk vessel equipped with a pressure release valve. After standing overnight at room temperature, the mixture was filtered and the solid washed twice with 10 mL heptane.

step b) reaction with the metallocene compound

A solution of the metallocene compound reported in table 2 in toluene (4 mL) was added to 200 mg of support prepared in step a). The mixture was heated to 60 °C and kept at this temperature for 1 h. In the case of Cp_2TiCl_2 , a dark green solid was obtained, the liquid phase having become colourless. The liquid phase was removed by decantation and the solid phase was washed with heptane (2 mL) and dried under a flow of argon at 60°C.

Preparation of the catalyst system, comparative examples I general procedure

step a) preparation of the support $\text{MgCl}_2/\text{AlR}_n(\text{OEt})_{3-n}$

The same procedure followed for the above step a) was used.

step b) reaction with metallocene compound

A solution of the metallocene compound reported in table 2 (20 μmol) in toluene (4 mL) was mixed with triisobutylaluminum (TIBAL) (100 μmol) to give a violet solution. After 1 h at room temperature, this solution was added to 200 mg of support prepared in step a) as indicated in table 1. The mixture was heated to 60 °C and kept at this temperature for 1 h, after which time a light green solid was obtained. In contrast to the experiments carried out without the catalyst/TIBAL precontact, the liquid phase was not colourless but remained violet. The liquid phase was removed by decantation and the solid phase was washed with heptane (2 mL) and dried under a flow of argon at 60°C.

Preparation of the catalyst system, comparative examples II general procedure

Preparation of non dealcoholated adduct of formula $\text{MgCl}_2.2.37\text{EtOH}$

Following the procedure described by Lee et al. in J. Molec. Catal. A 191, 2003, 155, magnesium chloride (9.52 g) was mixed with ethanol (100 mL) and stirred at 60 °C until dissolved. n-Decane (100 mL) was then added and the mixture stirred at (nominally) 2000 rpm under vacuum at 80 °C. As described by Lee, precipitation was observed as the ethanol evaporated. The solid product was separated by decantation and washed first with toluene (50 mL) and subsequently petroleum ether (40-70 fraction; 2 x 20 mL), then dried under vacuum (1 mbar) for 20 min. to give a fine, free-flowing powder.

Determination of the ethanol content of the product, using a GC method, described above indicated the composition: $\text{MgCl}_2.2.37\text{EtOH}$.

step a) preparation of the support $\text{MgCl}_2/\text{AlEt}_n(\text{OEt})_{3-n}$

10 mL *n*-heptane were added to 1 g of the $\text{MgCl}_2.2.37\text{EtOH}$ support obtained as described above under argon and the mixture was cooled to 0 °C. AlEt_3 (25 wt-% solution in toluene) was then added gradually, over 5-10 min., to give a mol ratio $\text{AlEt}_3/\text{EtOH} = 2$, the reaction being carried out in a standard Schlenk vessel equipped with a pressure release valve. The

mixture was allowed to warm slowly to room temperature and reaction was continued with occasional agitation for a further 2 days. The resulting support was isolated by filtration, washed with heptane and petroleum ether (40-70) and then dried under a flow of argon and subsequently in vacuum.

step b) reaction with metallocene compound

A bright red solution of Cp_2TiCl_2 (20 μmol) in toluene (4 mL) was added to 200 mg of the above $\text{MgCl}_2/\text{Et}_n\text{Al}(\text{OEt})_{3-n}$ support and the mixture heated to 60 °C and kept at this temperature for 1 h, after which time a green solid was obtained, the liquid phase having become colorless. The liquid phase was removed by decantation and the solid was dried under a flow of argon at 60°C. The green color of the immobilized catalyst was less intense than observed in the examples given in table 2.

step b) reaction with metallocene compound previously treated with TIBAL ($\text{Al}^{\text{i}}\text{Bu}_3$)

A bright red solution of Cp_2TiCl_2 (20 μmol) in toluene (4 mL) was mixed with $\text{Al}^{\text{i}}\text{Bu}_3$ (100 μmol), resulting in an immediate change of color to give a violet solution. After 1 h at room temperature, this solution was added to 200 mg of the above $\text{MgCl}_2/\text{Et}_n\text{Al}(\text{OEt})_{3-n}$ support and the mixture heated to 60 °C and kept at this temperature for 1 h, after which time a light green solid was obtained. In contrast to the experiment carried out without the catalyst/ $\text{Al}^{\text{i}}\text{Bu}_3$ precontact, the liquid phase was not colorless but remained violet. After removal of the liquid phase by decantation and washing with heptane (2 mL) the solid was dried under a flow of argon at 60°C. The results of the polymerization runs are reported in table 3.

Polymerization, general procedures

Polymerization runs 1 – 12 in table 2 were carried out in a 200 mL Büchi reactor equipped with a hollow-shaft turbine stirrer. 100 mg of immobilized catalyst was charged to the reactor, followed by 100 mL of heptane containing 1 mmol triisobutylaluminium (TIBAL). The reactor contents were heated in 5 min. to 50 °C at an ethylene overpressure pressure of 0.1 MPa, after which the monomer pressure was increased to 0.5 MPa and kept constant for 45 min. The stirrer rate was approx. 1200 rpm. After venting the reactor, the polymer slurry was mixed with 20 mL ethanol containing 9 % HCl, followed by 200 mL 1M HCl_{aq} , and stirred for 20 min. The polymer was recovered by filtration, washed with water (3 x 200 mL) and ethanol (2 x 30 mL) and dried in vacuum overnight at 70 °C.

All other polymerization runs in tables 2 and 3 were carried out in a 1 L Premex autoclave equipped with a Vortex stirrer. Petroleum ether (40-70, 450 mL) was introduced via a

canulla. The reactor contents were stirred and heated to 50 °C. Triisobutylaluminium (TIBAL, 1 mmol) in petroleum ether (40-70, 10 mL) was introduced via the catalyst injection system. An ethylene overpressure of 0.1 MPa was applied and stirring continued for 5-10 min. A slurry of the immobilized catalyst (100 mg) in petroleum ether (40-70, 10 mL) was introduced through the catalyst injection system, which was then flushed with a further 50 mL petroleum ether (40-70). The ethylene pressure was increased to 1 MPa and kept constant for 2 h at a polymerization temperature of 50 °C, the stirrer speed being ca. 1000 rpm. Polymerization was terminated by injection of 20 mL methanol. After venting the reactor, the polymer was isolated as described above.

The polymerization results are reported in tables 2 and 3.

Molecular weights and molecular weight distributions of the resulting polymers were determined by high temperature GPC (PL-GPC210) at 135 °C using 1,2,4-trichlorobenzene as solvent.

Table 1.

Support	Starting material	organo-aluminium compound	solvent	Al/EtOH molar ratio
A	MgCl ₂ .1.1 EtOH	AlEt ₃	toluene	2
B	MgCl ₂ .1.1 EtOH	Al <i>i</i> Bu ₃	hexane	2
C	MgCl ₂ .2.1 EtOH	AlEt ₃	toluene	2
D	MgCl ₂ .2.1 EtOH	Al <i>i</i> Bu ₃	hexane	2
E	MgCl ₂ .2.1 EtOH	AlEt ₂ Cl	toluene	3
F	MgCl ₂ .2.8 EtOH	AlEt ₃	toluene	2
G	MgCl ₂ .2.8 EtOH	Al <i>i</i> Bu ₃	hexane	2
H*	MgCl ₂ .2.37EtOH	AlEt ₃	toluene	2

*comparative (non dehalcolated)

table 1 continued

Support	Al, wt-%	OEt, wt.-%	Overall composition	Surface area
A	4.10	4.9	MgCl ₂ .0.18AlEt _{2.28} (OEt) _{0.72}	39 m ² /g
B	2.81	3.1	MgCl ₂ .0.12Al <i>i</i> Bu _{2.34} (OEt) _{0.66}	n.a.
C	4.80	5.6	MgCl ₂ .0.22AlEt _{2.31} (OEt) _{0.69}	373 m ² /g
D	2.92	3.8	MgCl ₂ .0.13Al <i>i</i> Bu _{2.22} (OEt) _{0.78}	n.a.
E	6.83	7.8	MgCl ₂ .0.36AlEt _{1.31} Cl(OEt) _{0.69}	n.a.
F	5.98	6.5	MgCl ₂ .0.29AlEt _{2.35} (OEt) _{0.65}	n.a.
G	4.14	4.6	MgCl ₂ .0.21Al <i>i</i> Bu _{2.33} (OEt) _{0.67}	n.a.
H*	n.a.	n.a.	n.a.	n.a.

* comparative (non dehalcolated magnesium alcohol adduct)

n.a. not available

table 2

Run	Support	titanocene	loading on support μmol/g	Activity kg/mol.b ar.h	M _w	M _w /M _n
1	A	Cp ₂ TiCl ₂	100	218	1181500	2.6
2	B	Cp ₂ TiCl ₂	100	207	728600	2.5
3	C	Cp ₂ TiCl ₂	100	327	1106000	2.7
4	C	Cp ₂ TiCl ₂	100	315	n.a.	n.a.
5	C	Cp ₂ TiCl ₂	100	320	n.a.	n.a.
6	C	Me ₂ Si(Me ₄ Cp)(N ^t B u)TiCl ₂	100	217	1113500	2.5
7	D	Cp ₂ TiCl ₂	100	268	1038500	2.0
8	E	Cp ₂ TiCl ₂	100	50	440300	2.1
9	F	Cp ₂ TiCl ₂	100	85	1000400	2.8
10	G	Cp ₂ TiCl ₂	100	89	963600	2.6
11	C	Cp ₂ ZrCl ₂	100	114	734700	2.4
12	C	<i>rac</i> -Et(Ind) ₂ ZrCl ₂	100	5	645400	2.1
13	C	Cp ₂ TiCl ₂	50	343	n.a.	n.a.
14	C	Cp ₂ TiCl ₂	25	432	n.a.	n.a.
15	C	Cp ₂ TiCl ₂	10	627	n.a.	n.a.
16	C	Cp[1,3-(2',6'- Me ₂ C ₆ H ₃) ₂ (CH ₂ N) ₂ C=N]TiCl ₂	100	201	n.a.	n.a.

Table 2 - continued

Run	Support	titanocene	loading on support	Activity	M _w	M _w /M _n
			μmol/g	kg/mol.b ar.h		
17	C	Cp[1,3-(2',6'-Me ₂ C ₆ H ₃) ₂ (CH ₂ N) ₂ C=N]TiCl ₂	5	1834	n.a.	n.a.
18	C	Me ₂ Si(Me ₄ Cp)(N ^t Bu)TiCl ₂	5	465	n.a.	n.a.
19	C	(^t Bu ₃ P=N)CpTiCl ₂	5	1230	n.a.	n.a.
20	A	Cp ₂ TiCl ₂	10	606*	619400	2.3
21	A	CpTiCl ₃	10	7510*	1081500	2.2
22	A	(^t BuCp)TiCl ₃	10	7520*	865400	2.4
23	A	(C ₅ H ₄ CMe ₂ Ph)TiCl ₃	10	7940*	503300	2.5

*polymerization time 1 hour

n.a. not available

table 3 comparative examples

Run	Support	Titanocene	loading on support μmol/g	Activity kg/mol.bar.h
3	C	Cp ₂ TiCl ₂	100	327
24 [§]	C	Cp ₂ TiCl ₂ ⁺	100	91
6	C	Me ₂ Si(Me ₄ Cp)(N ^t Bu)TiCl ₂	100	217
25 [§]	C	Me ₂ Si(Me ₄ Cp)(N ^t Bu)TiCl ₂ ⁺	100	183
16	C	Cp[1,3-(2',6'-Me ₂ C ₆ H ₃) ₂ (CH ₂ N) ₂ C=N]TiCl ₂	100	201
26 [§]	C	Cp[1,3-(2',6'-Me ₂ C ₆ H ₃) ₂ (CH ₂ N) ₂ C=N]TiCl ₂ ⁺	100	47
27 [§]	C	<i>rac</i> -Et(Ind) ₂ ZrCl ₂	100	8
28 [§]	C	<i>rac</i> -Et(Ind) ₂ ZrCl ₂ ⁺	100	20
29 [§]	H	Cp ₂ TiCl ₂	100	262
30 [§]	H	Cp ₂ TiCl ₂ ⁺	100	25

+precontacted with TIBA

§ comparative example

From the above table clearly results that the polymerization activity of the titanium-based catalyst system obtained according to the process of the present invention is higher than the activity of a similar catalyst system wherein the titanocene is pretreated with an organoaluminum compound such as TIBA. From the above table also results that this effect is achieved only when a titanium-based catalyst system is used, while for the zirconium-based catalyst the improvement of the activity due to the avoidance of the pretreatment with TIBA is not present (see entries 27 and 28). Moreover when a non dealcholated magnesium chloride is used the activity of the titanocene-based catalyst results to be lower (see entries 29 and 30 in which the support H is used).